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THE CHEMISTRY CONTROLLING IGNITION OF HYDROCARBONS AND THEIR MIXTURES AT HIGH PRESSURES

Contract No. DAAG55-98-1-0286; 37699-EG
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SUMMARY/OVERVIEW:

This research program investigates the chemistry controlling ignition of hydrocarbons and their mixtures at elevated pressures. The objective of this program is the development of kinetic and mechanistic information in the low and intermediate temperature regime (600-1000 K) over a range of pressures (up to 20 atm). The methodology is to perform bench scale tests on single component pure fuels; on 2, 3, and 4 component mixtures of pure fuels; and on full boiling range fuels. The experiments are being carried out over a range of reaction conditions that are representative of actual engine conditions prior to and during the ignition process. Results from these studies will be used to provide kinetic and mechanistic information, to formulate hypotheses on autoignition mechanisms, to determine the relative effects of the various classes of components within multi-component fuel mixtures, and to provide combustion models that can be used in the design and evaluation of engine systems.

TECHNICAL DISCUSSION:

Efforts during this year focused on three specific research areas, the first was the oxidation of n-heptane and iso-octane in the Pressurized Flow Reactor (PFR) at Drexel. The second was the development of methods (GC and GC/MS) for the separation, identification, and quantification of large numbers of intermediate oxidation species. The third was part of a related AASERT program (DAAG55-97-1-0196) in which a technique for the spectral separation of radical from non-radical species using Magneto-Optic Rotation (MOR) coupled to Cavity Ringdown Laser Absorption Spectroscopy (CRLAS) has been developed and tested successfully. Efforts for next year will focus on the identification and quantification of intermediate species from 1-pentene, n-heptane, iso-octane, toluene, and their mixtures and the application of the diagnostic techniques. Furthermore, our efforts to develop a chemical surrogate for JP-8 will continue.

Hydrocarbon Mixtures -- Last year, we identified that JP-8 exhibited Negative Temperature Coefficient (NTC) behavior. This behavior occurs when the reactivity of a hydrocarbon species decreases with increasing temperature, something contrary to intuition. This behavior can be characterized utilizing a CO reactivity mapping technique. The resulting CO reactivity map for JP-8 had similar trends, namely temperature of maximum reactivity and peak shape, as other previously investigated Industry Standard Fuels (ISF) and simplified blends.

Therefore, this year's work focused on the detailed speciation of these simplified blends, specifically RON 92. RON 92 was developed at Drexel University two years ago by blending n-heptane, iso-octane, 1-pentene, and toluene. This blend exhibited NTC behavior similar to ISFs. n-Heptane and iso-octane were oxidized in our Pressurized Flow Reactor (PFR) to identify the existence of a Negative Temperature Coefficient (NTC) region and to indicate temperatures where detailed speciation experiments should be conducted. Utilizing the CO reactivity mapping technique, NTC behavior was observed for n-heptane and iso-octane. Initially plans were made to use the same operating conditions for the individual hydrocarbons and their mixtures to facilitate comparison. However, due to the differences in reactivity and heat release, this was not possible. The first experiments were with n-heptane at a pressure of 8 atm, equivalence ratio of 0.4, nitrogen dilution of 85%, and residence time of 100 ms. As the reactor cooled from 800 K to 625 K, a clear NTC behavior was observed [Figure 1]. The temperature at which the reactivity peaked, referred to as the start of NTC, occurred at 705 K. Next, iso-octane was oxidized at a pressure of 8 atm, equivalence ratio of 0.6, nitrogen dilution of 62%. Again, as the reactor cooled from 800 K to 625 K, NTC behavior was observed, the start of which occurred at 665 K [Figure 1]. Efforts are now under way to determine why iso-octane NTC behavior occurred at the lower temperatures. Furthermore, measurements of species formed during the oxidation of n-heptane are under way. Experiments with the RON 92 blend will be conducted shortly.

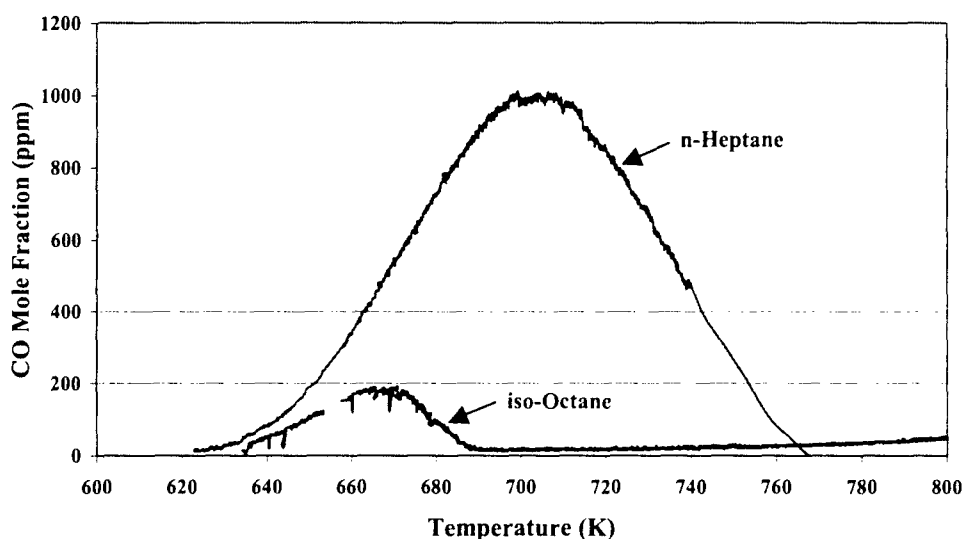


Figure 1: CO Reactivity mapping for n-heptane and iso-octane

Species Identification -- The direction for this year was to obtain detailed speciation for each of the individual hydrocarbons and for their mixture as RON 92. In order to accomplish this task, a gas chromatographic technique capable of separating the large number of intermediate oxidation species expected from RON 92 had to be developed. The technique developed utilizes a single gas chromatograph (GC) column that is initially cooled to -20°C and slowly raised to higher temperatures. While this technique can separate large numbers of both large and small hydrocarbons, it requires a substantial amount of time (approximately 80 minutes per sample). Thus, development of techniques that can improve separation while minimizing the time required will continue. After separation, the compounds still need to be identified and quantified. Initially plans were to use a Fourier Transform Infrared (FT-IR) spectrometer for this purpose. However, upon coupling the GC to the FT-IR and using the desired separation technique, the FT-

IR did not have a sufficiently low detectability limit for the important species. As a result, the GC was then coupled with a shared use Mass Spectrometer (MS) in the Chemistry Department. Since this particular MS was used for identification of high molecular mass and high concentration samples, the instrument had to be tuned for low molecular weight and low concentration samples. The MS system has now been thoroughly tested with our GC method and it has the required sensitivity. It is also equipped with the NIST MS spectral library for identification of the oxidation species.

Laser Diagnostics -- In the related AASERT program, we have been developing advanced laser diagnostics techniques for measuring radical and stable species in combustion environments. Previously, we adapted the sensitive technique of Cavity Ringdown Laser Absorption Spectroscopy (CRLAS) and the selective technique of Magneto-Optic Rotation (MOR) to measuring highly reactive radicals in flame environments. This year, we continued to refine both the MOR and CRLAS techniques and began to couple CRLAS and MOR, developing a technique dubbed Cavity Enhanced Magneto-Optic Rotation (CEMOR). Refining MOR, we conducted experiments investigating concentration and experimental configuration effects on MOR with two weakly paramagnetic species, gallium and calcium, seeded into an air-acetylene flame. We observed absorption and MOR spectra of both calcium and gallium and determined sensitivity limits and optimal laser configuration. Lower detection limits were approximately 40 ppm and 50 ppb for gallium and calcium, respectively. Next, we investigated the absorption and MOR spectra of tellurium isotope 130, a non-paramagnetic species, and calcium in the blue region of the visible spectrum (420-425 nm). While detection of the Ca absorption line among the Te lines was very difficult using standard absorption techniques [Figure 2], MOR enabled selective observation of the weakly paramagnetic calcium [Figure 3]. The MOR technique will greatly expand our ability to identify and quantify radical species in regions of the electromagnetic spectrum congested by multiple stable species with multiple lines by virtually eliminating the signals from these species.

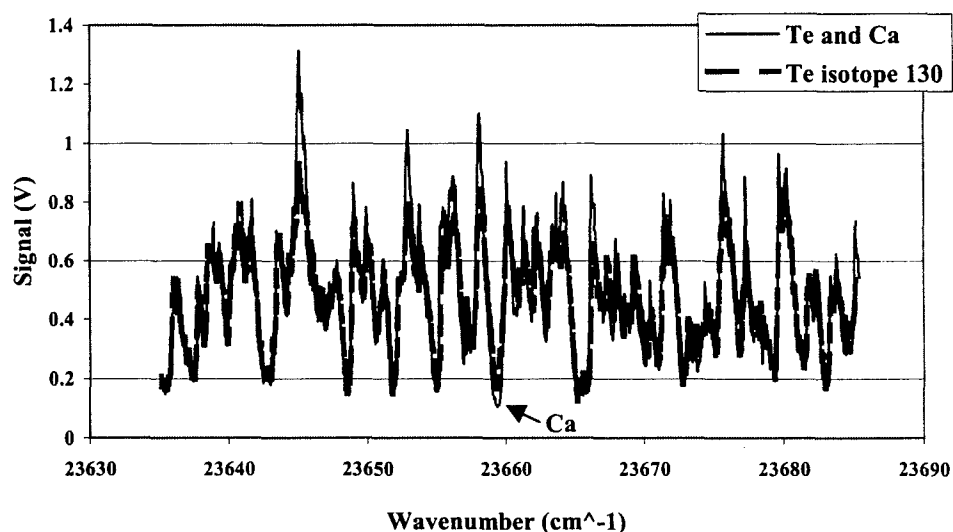


Figure 2. Absorption spectra of Te isotope 130 and Ca.

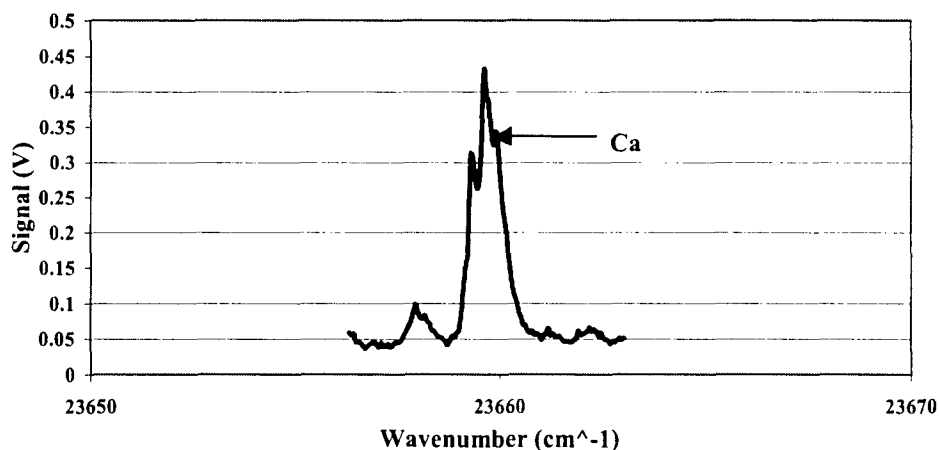


Figure 3. MOR spectra of Te isotope 130 and Ca.

Coupling the MOR technique within a CRLAS setup resulted in the developed of Cavity Enhanced Magneto-Optical Rotation (CEMOR). The resulting technique is capable of selectively detecting paramagnetic species even at extremely low concentrations. The polarized light enters the cavity where it interacts with the analyte, where a fraction of the light is absorbed and the remainder is rotated by a small amount. The rotation and adsorption of the light increases with each pass through the cavity, appearing as a maximum immediately before cavity losses overcome further rotation increases. The tail end of this signal appears similar to a ringdown absorption curve. Characterization of the CEMOR signal as a function of both cavity losses and rotation effects will enable us to use this technique for quantitative measurements. Initial efforts to characterize these effects have been accomplished utilizing gallium in an air-acetylene flame. In experiments spanning a range of gallium concentrations, we observed that the time to the maximum signal occurs earlier for higher concentrations [Figure 4]. These initial observations indicate that the time associated with this maximum could be used to determine concentration. Further investigation of this technique and modeling of the effect is required for a more precise quantification and identification of species. CEMOR is very promising for study of radical species, as it allows the detection of trace quantities using IR regions with multiple absorbers.

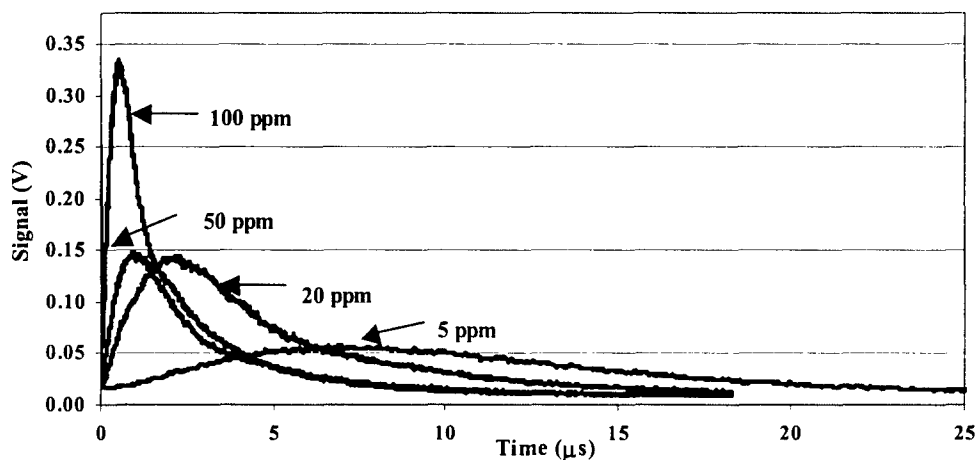


Figure 4. CEMOR signal of Gallium in air-acetylene flame, 417.204 nm.